Photochemical Sinks of Organic Pollutants in Estuarine and Near-Shore Environments

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LONG-TERM GOALS

A principal objective of this work is to assess the quantitative importance of homogeneous and heterogeneous photochemistry as a sink of pollutants in the aquatic environment. In particular, we ultimately hope to develop a predictive model for the photochemical degradation of hydrophobic organic pollutants (HOPs) in natural waters, based on correlations between the redox properties of selected series of HOPs and the rates and wavelength dependence of their heterogeneous photodegradation by colored dissolved organic matter (CDOM).
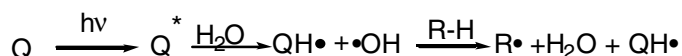
OBJECTIVES

Our principal near-term objectives for this project were as follows:

- Complete a study examining the photoproduction of the hydrated electron ($e^-_{(aq)}$), a strong reductant, by isolated humic substances and by CDOM in natural waters. The objectives of this study were 1) to quantify the magnitude and wavelength dependence of $e^-_{(aq)}$ production, 2) to examine the variability of this production among different sources of CDOM, and 3) to compare the magnitude of $e^-_{(aq)}$ production to past estimates acquired using laser flash photolysis and to the photochemical production of H_2O_2.

- Perform a preliminary study characterizing the reducing potential of reductants that are produced photochemically by the CDOM.

- Develop an improved understanding of the mechanism by which benzoquinones and quinoidal components of CDOM photochemically oxidize organic substances under aqueous conditions (Vaughan and Blough, 1998). Earlier work has shown that the initial photochemical event when
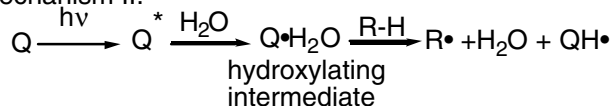
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benzoquinone derivatives are photolyzed in aqueous media is a very rapid interaction with a water molecule. The variety of models that have been proposed for this process can be summed up with two limiting mechanisms. The first holds that the photoexcited quinone directly oxidizes a water molecule forming one hydroxyl radical (•OH) and one semiquinone radical (QH•). In this case it is the free hydroxyl radical which subsequently oxidizes the organic substances. The other limiting mechanism postulates a "hydroxylating intermediate" (Q•H$_2$O), which could be considered a charge transfer complex between water and the photoexcited quinone. This intermediate interacts with and oxidizes the organic substrate and generates the semiquinone, or else it reverts to the ground state reactants.

Mechanism I:

$$Q \xrightarrow{h\nu} Q^* \xrightarrow{H_2O} QH\bullet + \bullet OH \xrightarrow{R\text{-}H} R\bullet + H_2O + QH\bullet$$

Mechanism II:

$$Q \xrightarrow{h\nu} Q^* \xrightarrow{H_2O} Q\bullet H_2O \xrightarrow{R\text{-}H} R\bullet + H_2O + QH\bullet$$
hydroxylating
intermediate

While both limiting mechanisms provide the same products (oxidized substrate and semiquinone), there are profound differences in the kinetic consequences of these two mechanisms, The free hydroxyl radical is known to react rapidly and indiscriminately with a wide variety of organic compounds (aromatics as well as aliphatics). In contrast the hydroxylating intermediate is predicted to react much more slowly with organic substrates and also show a higher degree of discrimination. Thus a comprehensive kinetic model for CDOM/ pollutant photochemistry requires that these pathways be distinguished.

APPROACH

To achieve the first objective, we have developed two new chemical trapping methods for determining $e^-_{(aq)}$. The first employs the rapid reaction of N_2O with the hydrated electron to form OH, followed by the reaction of OH with dimethylsulfoxide to generate a methyl radical, which is then trapped by an amino-nitroxide; following derivatization with fluorescamine this product is separated by reversed-phase high performance liquid chromatography and quantified fluorometrically (see for example, Kieber and Blough, 1990; Li et al., 1997; Vaughan and Blough, 1998). The second employs the rapid reaction of $e^-_{(aq)}$ with monochloromethane to produce the methyl radical directly, which is then trapped by the nitroxide and analysed as above.

Our studies (see below) have shown that the rates of $e^-_{(aq)}$ formation are far smaller than those for O_2^- and H_2O_2. This result indicates the presence of a significant additional pool of reducing intermediate(s). Other than the ability of this pool to reduce O_2 to O_2^-, nothing is known about its capability of reducing pollutants. To map the photoreducing potential of the CDOM, chloromethane, bromomethane and iodomethane as well as a series of mono-, di-, tri- and tetrachlorinated compounds (monochloromethane, dichloromethane, chloroform and carbon tetrachloride) have been or are currently

being examined. Because increasing halogen substitution makes these compounds easier to reduce, the yield of carbon-centered radicals produced by one-electron reduction (and determined by nitroxide trapping) is anticipated to increase with increasing halogen substitution, if the photochemical equivalents generated within the CDOM are sufficiently reducing.

To address our third objective, we have carried out a series of laser flash photolysis (LFP) investigations aimed at determining the intermediate produced upon excitation of quinones in aqueous solution. Our approach is predicated on the reasoning that if mechanism (I) is operative, then QH• should be formed rapidly (<10 ns) when benzoquinone derivatives are photoexcited in aqueous solution. Likewise this mechanism leads to the prediction that upon adding water to a nonreactive solvent, the excited triplet state of the quinone should be quenched directly to yield semiquinone radical. On the other hand mechanism (II) predicts that photoexcitation of the quinone will not immediately generate QH•, but instead will produce a new intermediate (Q•HOH) which will convert to QH• only when an oxidizable organic compound is added to the solution.

WORK COMPLETED

1) A major study of the photoproduction of $e^-_{(aq)}$ by humic substances and by CDOM in natural waters has been completed and is being prepared for publication (Thomas-Smith and Blough, 2000). These results will be presented at the PacificChem Conference in December 2000. Salient results are provided below.

2) A study of the ability of CDOM to photoreduce chloromethane, bromomethane and iodomethane has been completed and the results will be presented at the PacificChem Conference in December 2000. Experiments employing other halogenated compounds are ongoing.

3) An extensive series of LFP experiments have been performed to examine the mechanism of quinone photochemistry. These results will be presented at the PacificChem Conference in December 2000.

RESULTS

Results from the $e^-_{(aq)}$ study can be summarized as follows: 1) Quantum yields for humic substances are ~ two orders of magnitude lower than those obtained in flash photolysis experiments, ranging from ~ $2x10^{-4}$ at 296 nm to ~$2x10^{-5}$ at 355 nm, indicating that past flash photolysis experiments were flawed by two photon effects; 2) Natural waters from the western shelf of south Florida exhibit quantum yields at 296 nm that are ~1 order of magnitude higher, but fall off with increasing wavelength more precipitously; 3) quantum yields in the Middle Atlantic Bight increase with decreasing absorption from the river inputs to the coast, suggesting the in situ formation of a material with a higher propensity to form $e^-_{(aq)}$; 4) quantum yields for $e^-_{(aq)}$ production are far lower than those for O_2^- and H_2O_2 production, indicating the presence of significant additional pools of reducing intermediate(s). These reducing intermediates, however, are not sufficiently strong to reductively dehalogenate bromomethane or iodomethane.

Although other quinones have been or are currently being examined, our LFP investigation has focused on toluquinone (methylbenzoquinone) as a representatve member of the benzoquinone family. LFP of this species (266 nm, 6 ns excitation) in aqueous solution (pH 7) gives the transient spectrum illustrated

in Fig. 1. The behavior is complex. In part this is due to the fact that many of the species that are generated have overlapping absorption bands. The fact that QH• can ionize to give its conjugate base Q¯• further complicates the spectra. An analysis of the time dependence of these spectra indicates that there are at least two kinetically distinct species. Initially following photoexcitation there is a broad absorption band that extends to >500 nm. Within 500 ns seconds this species decays and is replaced with a longer-lived intermediate. The latter has a sharper profile than the first intermediate.
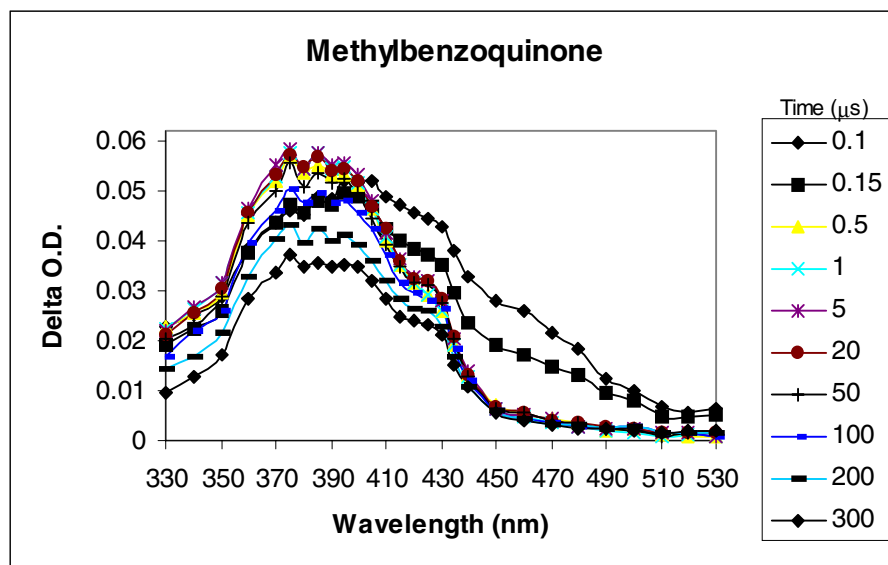

Figure 1. Time-resolved absorption spectra following laser excitation of methylbenzoquinone in water.

A clearer understanding of the LFP behavior of photoexcited quinones in aqueous media requires that reference spectra for the potential intermediates (eg., the semiquinone anion, the protonated semiquinone, and the excited triplet state) be carefully characterized. Therefore we are continuing to rigorously characterize the spectra of the relevant intermediates under conditions where only one of them is produced.

IMPACT/APPLICATIONS

Knowledge of the rates and mechanisms of removal of pollutants from the environment is critical for establishing their long-term impact on aquatic ecosystems. Unfortunately, because of the diverse suite of compounds released, it is usually infeasible to assess the quantitative importance of all sinks for every compound. Moreover, new compounds are being created on a daily basis. A solution to this problem resides in the ability to predict the behavior of broad classes of compounds based on unifying chemical principles. Such an approach is being applied in this study. The development of robust relationships between the environmental rates of the CDOM-sensitized photodegradation of HOPs and the more readily-acquired molecular properties of the HOPs such as redox potentials and/or singlet energies may allow us to produce models capable of predicting the photochemical fate of HOPs in natural waters. These simple models could then be integrated into ecosystem-wide HOP fate models to improve our ability to predict HOP distribution and loss.

RELATED PROJECTS

In a related, ONR-supported project, we are examining the factors controlling the distribution and dynamics of CDOM in estuarine and coastal waters through a combination of field and laboratory measurements. As CDOM is the principal photoreactive constituent of most natural waters, an understanding of the factors which control its distribution in the environment is essential for determining the impact of photochemical processes in the remineralization of both natural and anthropogenic compounds.

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